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(54) Title: REMOVAL OF MERCAPTANS FROM HYDROCARBON STREAMS USING IONIC LIQUIDS

(57) Abstract: Methods for removing mercaptans from hydrocarbons streams, for example crude oil and natural gas, are provided. The methods use basic metal salts which react with mercaptans to form mercaptides. The metal salts are dissolved or suspended in ionic liquids, which tend to have virtually no vapor pressure. After the mercaptides are adsorbed into the ionic liquid, the demercaptanized hydrocarbon stream can be removed, for example by distillation, decantation or gravity separation. Then the mercaptides can be oxidized, for example, by exposure to air, to form disulfides. The disulfides are insoluble in the ionic liquids, and can be readily removed. Sodium hydroxide is a preferred salt. Non-water reactive ionic liquids are preferred. The mercaptan-containing hydrocarbon stream can be in the gas phase or in the liquid phase. The flow of hydrocarbon stream over/through the ionic liquid can be for example, co-current, counter-current, or staged in stirred tanks, with countercurrent being preferred.

distilled, the mercaptans removed, and the product blended with the crude. This option requires using expensive distillation facilities to remove the light portion of the crude.

The oxidation of the mercaptides to disulfides and regenerated caustic can be done with a variety of oxidants (air, pure oxygen, enriched air, chemical oxidants such as hydrogen peroxide) or mixtures thereof. However, air is the most commonly used oxidant because of its low cost. The 5 oxidation of the mercaptides can be done without a catalyst, but the reaction tends to be slow. It is generally preferred to incorporate a catalyst to accelerate the oxidation of the mercaptides. These catalysts are typically metals, and the most common metals are lead (typically as PbS), copper (typically as a copper chloride), or a phthalocyanine complex of copper, iron, nickel or cobalt, preferably cobalt. The preparation and use of phthalocyanine complexes for mercaptan oxidation is 10 described in U.S. Pat. No. 5,880,279; U.S. Pat. No. 5,849,656, U.S. Pat. No. 5,741,415, and U.S. Pat No. 5,683,574 to Mazgarov et al. A particularly effective phthalocyanine complex involves cobalt phthalocyanine complexes with electron withdrawing substituents on the phthalocyanine ring. Particularly effective electron withdrawing substituents include a halogen (preferably 15 chlorine) and sulfate groups as described in U.S. Pat. No. 5,880,279.

The extraction of the mercaptans and the oxidation of the mercaptides can be done in one or two stages. The advantage of the use of one stage is primarily lower cost, but the disadvantages include the mixing of the oxidant and petroleum product, and the blending of the mercaptan reaction product disulfides with the petroleum product. The advantages of use to two separate 20 stages is the avoidance of mixing the oxidant and the petroleum product, and the separation of the disulfide reaction product, but the disadvantage is higher cost.

Mercaptans can be removed from whole crudes by contacting the crude oil with a caustic mixture that includes a cobalt phthalocyanine complex and air, as described in U.S. Pat No. 5,683,574. The cobalt phthalocyanine complexes are selected to avoid formation of emulsions. 25 The caustic/cobalt phthalocyanine solution simultaneously adsorbs the mercaptans and reacts them to form disulfides, which remain in the crude. The caustic and phthalocyanine complexes can be partially recovered using a separation system. However, this technology has various technical limitations. For example, the introduction of air directly in with the crude causes concerns over safety, and when nitrogen from the air is released from the crude, light (C₄-) hydrocarbons are also purged. This not only results in a loss of crude, but also causes a safety hazard and a disposal 30 problem. Also, since the reaction is essentially stoichiometric, the amount of caustic and cobalt catalyst that must be used increases, often to the point where it is not economically viable to treat the crude.

Brief Description of the Drawings

Figure 1 is a schematic illustration of a mercaptan removal process using the method described herein.

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Detailed Description of the Invention

Methods for removing mercaptans from hydrocarbon streams, preferably crude oil, are provided. As used herein, the term "adsorption" is used to describe the movement of mercaptans out of hydrocarbon streams and into ionic liquids in the form of mercaptides.

10

Mercaptans

Mercaptans are C₁₋₅₀ mercaptans (carbon-containing compounds that contain a -SH group), more preferably C₁₋₁₀ (cyclic, linear, branched and aromatic) mercaptans. They may include other functional groups, such as hydroxy groups, carboxylic acid groups, heteroatoms, and the like, provided that such groups do not react with either the base (typically sodium hydroxide) or the ionic liquid.

15

Hydrocarbon Feedstreams

The hydrocarbon feedstreams include crude oil feedstreams and natural gas feedstreams. The hydrocarbon stream can include a C₆- fraction. The hydrocarbon stream can include more than about 50% by weight methane, ethane, propane, butane or combinations thereof.

Where the hydrocarbon feedstreams include relatively high levels of sulfur impurities, and the feedstream is amenable to hydrotreatment or other means well known to those of skill in the art, such as extractive Merox, such methods can be used to reduce the level of sulfur impurities, and residual mercaptans can be removed using the methods described herein.

25

Basic Salts

The basic salts can be virtually any base capable of reacting with mercaptans to form mercaptides. Examples include alkali metal and alkaline earth hydroxides, carbonates and bicarbonates. Sodium hydroxide is a preferred basic salt.

30

The concentration of the basic salt in the ionic liquid is typically at least about 0.5 moles of salt per liter of solvent, and preferably at least about 2 moles of salt per liter of solvent.

It does not matter whether the salts are dissolved or merely suspended in the ionic liquids for them to function as intended. It is preferred, however, to select combinations of ionic liquids

for example, straight, branched, or cyclic alkyl groups, preferably a methyl group, alkyl chains containing a terminal alcohol group, alkyl groups containing heteroatoms such as oxygen, nitrogen and/or sulfur. The substituents can be in any position on the heteroaromatic ring, but in the case of pyridine, is preferably in the para (or 4) position.

5 These rings can alkylated with virtually any straight, branched or cyclic C₁₋₂₀ alkyl group, but preferably the alkyl groups are C₁₋₁₆ groups, since groups larger than this tend to produce low melting solids rather than ionic liquids. Various triarylphosphines, thioethers, and cyclic and non-cyclic quaternary ammonium salts have also been used. Counterions which have been used include chloroaluminate, bromoaluminate, gallium chloride, tetrafluoroborate, tetrachloroborate, 10 hexafluorophosphate, nitrate, trifluoromethane sulfonate, methylsulfonate, p-toluenesulfonate, hexafluoroantimonate, hexafluoroarsenate, tetrachloroaluminate, tetrabromoaluminate, perchlorate, hydroxide ion, copper dichloride anion, iron trichloride anion, zinc trichloride anion, as well as various lanthanum, potassium, lithium, nickel, cobalt, manganese, and other metal ions.

15 Certain low melting solids can also be used in place of ionic liquids, depending on the particular separation to be effected. Low melting solids are generally similar to ionic liquids but have melting points between room temperature and about 212°C or are liquid under the process conditions. The use of low melting solids can be preferred if the density of the products and the ionic liquid are similar and it becomes difficult to phase separate products from the ionic liquids. In such a case, the low melting solid can be crystallized and separated from the products. As used 20 herein, the term "ionic liquid" is intended to include low melting solids unless otherwise specified.

25 The ionic liquids can either be neutral, acidic or basic. However, relatively acidic ionic liquids (chloroaluminate salts) tend to be water-reactive, whereas neutral ionic liquids (for example, tetrafluoroborate or hexafluorophosphate salts) tend to be non-water reactive. Since water is generated, it can be preferable to use non-water reactive ionic liquids, particularly if large amounts of mercaptans are to be removed. Neutral ionic liquids are also preferred if the hydrocarbon stream includes acid-sensitive components, for example normal alpha olefins, which are prone to isomerization.

30 In one embodiment, a library of ionic liquids is prepared, for example by preparing various alkyl derivatives of the quaternary ammonium cation, and/or varying the associated anions. The acidity of the ionic liquids can be adjusted, for example by varying the molar equivalents and combinations of Lewis acids.

Methods for Removing Mercaptans from Hydrocarbon Streams

The methods involve forming a solution of a basic metal salt such as sodium hydroxide in

ionic liquid. Accordingly, distillation, preferably under reduced pressure, is a preferred method for removing the water. Alternatively, if the mercaptide is not particularly soluble in the reaction water, the reaction water can be removed before the oxidation step. The basic metal salt can be kept reasonably concentrated in the ionic liquid without unwanted dilution in water using the
5 methods described herein.

The mercaptan-containing hydrocarbon stream can be in the gas phase or in the liquid phase. The flow of hydrocarbon stream over/through the ionic liquid can be, for example, co-current, counter-current, or staged in stirred tanks, with countercurrent being preferred.
10 The method is shown in more detail in Figure 1. As shown in Figure 1, a hydrocarbon with mercaptan (RSH) impurities is introduced to a contactor (10) that contains a non-water reactive ionic liquid and caustic. The resulting mercaptide is then either dispersed or dissolved in the ionic liquid, precipitated, or dissolved in the resulting aqueous phase. The reaction mixture is sent to a separator (20) where a purified hydrocarbon stream can be separated. The ionic liquid and,
15 optionally, reaction water are sent to an oxidation reactor (30) where disulfide is formed and caustic is regenerated. The disulfide and reaction water can then be removed, regenerating the ionic liquid and caustic. The regenerated ionic liquid and caustic are then recycled to the contactor (10).

Combinatorial Chemistry Approaches

20 A combinatorial approach can be used to identify optimum ionic liquids and/or basic salts for removing mercaptans from various hydrocarbon streams. An advantage to the combinatorial approach is that the choice of ionic liquid, basic salt and the like can be tailored to specific applications.

25 The scale of the mercaptan removal in combinatorial chemistry is preferably in the range of about 1 mg to 200 g, more preferably between one mg and 10 g, although the scale can be modified as desired depending on the equipment used. Those of skill in the art can readily determine appropriate sets of reactions and reaction conditions to generate and/or evaluate the libraries of interest.

30 The ionic liquids can be laid out in a logical fashion in multi-tube arrays or multi-well plates in the form of arrays of ionic liquids. Preferably, the ionic liquids all have a central core structure and have various modifications that permit the identification of structure-activity relationships with which to determine optimum compounds for a particular use. The basic metal salts or combinations thereof can also be laid out in a logical fashion, for example in arrays. In a preferred embodiment, an A x B array is prepared with various combinations of ionic liquids and

desulfurized hydrocarbon stream is removed. This can be done, for example, by covering the tubes with a rubber septum to avoid contamination, and adding the reagents via injection.

In one embodiment, the mercaptan removal is carried out via computer control. The identity of each of the ionic liquids and basic metal salts can be stored in a computer in a "memory map" or other means for correlating the data regarding the chemical reactions to the ionic liquids in the multi-tube racks or multi-well plates.

Alternatively, the chemistry can be performed manually, preferably in multi-tube racks or multi-well plates, and the information stored, for example on a computer.

Any type of multi-well plate or multi-tube array commonly used in combinatorial chemistry can be used. Preferably, the number of wells or tubes is in excess of 30, and there is a tube in at least 60 percent of the positions in each multi-tube array. The shape of the rack is not important, but preferably, the rack is square or rectangular. The tubes can be made, for example, from plastic, polymers, glass or metal such as stainless steel, depending on the type of anions used in the ionic liquid or in the metal salt.

Any type of liquid handler that can add reagents to, or remove reagents from, the wells and/or tubes can be used. Suitable liquid handlers are prepared, for example by Tecan. Many involve the use of robotic arms and robotic devices. Suitable devices are well known to those of skill in the art of combinatorial chemistry, and include those by Zymart, Gilson, Hamilton, Bodhan and Tecan.

Any device that can take samples from the individual wells and/or tubes and analyze the resulting hydrocarbon phase can be used. Preferably, the device is a chromatographic device such as an analytical or preparative scale HPLC, GC or column chromatography, although other devices can be envisioned depending on the chemistry performed. Since the ionic liquid is non-volatile, the sample is preferably taken from the hydrocarbon phase, which is immiscible with the ionic liquid.

Preferably, in those embodiments in which a chromatographic column (HPLC, GC or column chromatography) is used, the device has the ability to identify when the compound of interest is eluting from the column. Various means have commonly been used to identify when compounds of interest are eluting from a column, including UV, IR, TLC, GC-MS, FID, NMR, ELSD, nitrogen detection and the like. Any of these means and others known to those of skill in the art can be used, alone or in combination. However, when petroleum chemistry is being evaluated, the product stream often does not include UV-active compounds. In this type of embodiment, the analytical equipment preferably includes an ELSD detector.

N-hexylpyridinium chloride ($\text{hexpyr}^+\text{Cl}^-$), although a higher reaction temperature (130°C) was required to achieve high yields.

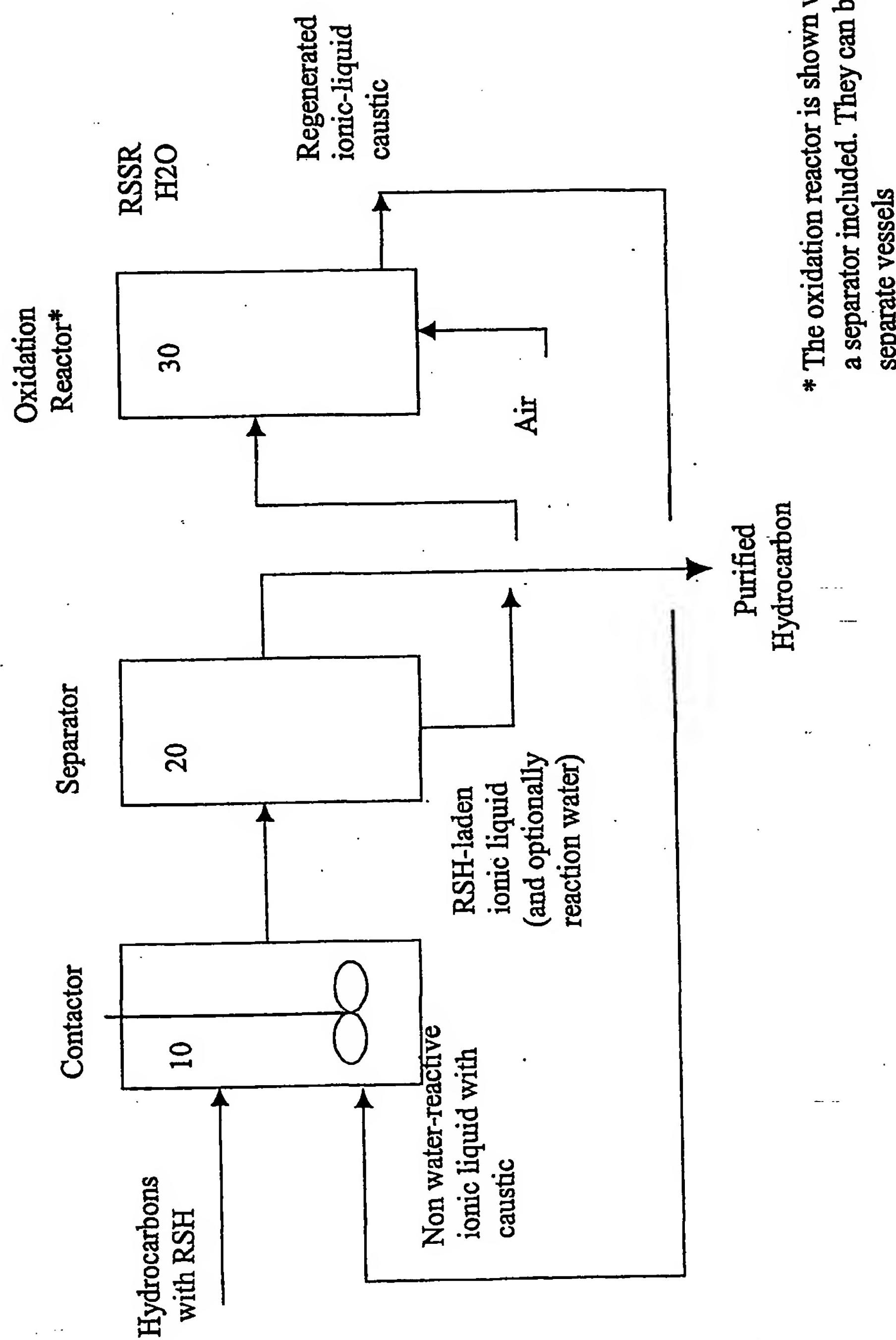
Two different procedures were used for conducting an anion exchange reaction to give a neutral ionic liquid. In one procedure, the precursor is dissolved in acetone and reacted with the sodium salt of the desired anion (NaBF_4 or NaPF_6). In the other procedure, the precursor is dissolved in water and reacted with the acid form of the anion (HBF_4 or HPF_6). The precursor hmim^+Cl^- was used make the ionic liquid $\text{hmim}^+\text{PF}_6^-$ by both procedures. The miscibility of the resulting ionic liquid with water was greatly influenced by the route of synthesis. The ionic liquid made by the acid route was immiscible with water, while the ionic liquid made using the sodium salt was miscible with water. While not wishing to be bound to a particular theory, it is believed that this change in miscibility with water is due to the presence of residual NaCl in the liquid made via the salt route.

The acid procedure was then used to generate a variety of ionic liquids using the precursors synthesized above, as well as additional precursors purchased from commercial suppliers. These reactions are summarized in Table 1. Not all of the combinations resulted in the formation of room temperature ionic liquids. Highly symmetric cations (Me_4N^+) and cations with long alkyl chains ($\text{C}_{16}\text{NMe}_3^+$) tend to give solid products with high melting points ($>100^\circ\text{C}$). The reactions that did not result in room temperature ionic liquids are shown in Table 2.

WHAT IS CLAIMED IS:

1. A method for removing mercaptans from hydrocarbon feedstreams comprising:
 - a) adding a mercaptan-containing hydrocarbon feedstream to an ionic liquid solution or dispersion of one or more basic metal salts to form mercaptides, where the mercaptides are either precipitated from solution or are dissolved or dispersed in the ionic liquid; and
 - b) separating the resulting de-mercaptanized hydrocarbon feedstream from the ionic liquid.
2. The method of claim 1, wherein the de-mercaptanized hydrocarbon feedstream is separated from the ionic liquid by distillation, decantation or gravity separation.
- 10 3. The method of claim 1, wherein the basic metal salts comprise an alkali metal or alkaline earth salt.
4. The method of claim 1, wherein the basic metal salts comprise sodium or potassium hydroxide.
5. The method of claim 1, wherein the ionic liquid is a non-water-reactive ionic liquid.
- 15 6. The method of claim 1, wherein the ionic liquid comprises tetrafluoroborate or hexafluorophosphate ions.
7. The method of claim 1, wherein the ionic liquid comprises quaternary amines with three or more methyl groups.
8. The method of claim 1, wherein the hydrocarbon stream comprises a C₆- fraction.
- 20 9. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight methane.
10. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight ethane.
- 25 11. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight propane.
12. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight butane.
13. The method of claim 1, wherein the hydrocarbon stream includes more than about 50% by weight LPG.
- 30 14. The method of claim 1, wherein the hydrocarbon feedstream is crude oil.
15. The method of claim 1, wherein the ionic liquid has a melting point at or below 100°C.
16. The method of claim 1, wherein the mercaptans comprise methyl and/or ethyl mercaptan.

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* The oxidation reactor is shown with a separator included. They can be separate vessels

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/s2211

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, P	US 6,274,026 A (SCHUCKER ET AL) 14 August 2001 (14/08/01), See entire document.	1-33